

Chapter 2

Concentrations of Sulfur and Nitrogen Species



Air pollutant concentrations measured in 1999 using the CASTNet filter packs are presented and analyzed in this chapter. Pollutant concentrations include SO_2 , SO_4^{2-} , HNO_3 , NH_4^+ , NO_3^- , and total nitrate (HNO_3 plus NO_3^- aerosol). Maps of 1999 annual mean concentrations are presented. Maps of 1999 SO_2 and nitrogen oxide (NO_x) emissions and maps of changes in emissions between 1990 and 1999 are also provided to add perspective to the concentration and deposition (Chapter 3) data.

The CASTNet data have been analyzed for trends using regressions and box plots. Annual and quarterly average concentrations measured at a subset of 34 eastern sites with the most complete historical record from 1990 through 1999 were analyzed for trends. Trends in annual SO_2 and NO_x emissions over the period 1990 through 1999 are also presented.

Quarterly and annual mean concentrations are presented in this chapter. Quarterly means were constructed from measured weekly filter concentrations. Quarterly means were calculated for all sites with at least eight valid weekly values. Annual means were calculated for all sites with at least three valid quarterly averages. Maps of annual means are presented directly in this chapter. Maps of quarterly means are provided in Appendix C.

Concentrations

Sulfur Dioxide

Figure 2-1 presents 1999 mean SO_2 concentrations. The map shows a large area extending from Illinois to eastern Tennessee to western New York with annual means above 5.0 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). Sand Mountain, AL (SND152) and Georgia Station, GA (GAS153) also had annual means above 5.0 $\mu\text{g}/\text{m}^3$. Sharp gradients in concentrations were observed from the Ohio Valley to New England and from the Ohio Valley to Wisconsin and Minnesota. The single highest concentration (20.8 $\mu\text{g}/\text{m}^3$) was observed at Quaker City, OH (QAK572). Western concentration data show no discernable pattern.

Figure 2-2 presents information on state-by-state total annual SO_2 emissions for 1999. The highest SO_2 emissions were estimated for states in the Ohio Valley, Texas, and Florida. The region with the highest SO_2 concentrations is related geographically with the emission inventory.

Particulate Sulfate

Annual mean SO_4^{2-} concentrations for 1999 are presented in Figure 2-3. The highest concentrations were observed from western Virginia and North Carolina across Kentucky, southern Indiana, and Tennessee, into Alabama and Georgia and also in eastern Ohio. The region with the highest annual mean sulfate concentrations in 1999 is located south of the region with the highest SO_2 concentrations shown in Figure 2-1.

Nitric Acid

Annual HNO_3 concentrations for 1999 are shown in Figure 2-4. Concentrations along the Appalachian Mountain chain were variable. The highest concentration was observed in eastern Ohio (QAK572) at 4.1 $\mu\text{g}/\text{m}^3$. The highest annual mean concentration in the west was 3.5 $\mu\text{g}/\text{m}^3$ at Joshua Tree National Monument (JOT403). Figure 2-5 provides a map of the United States NO_x emissions for 1999.

Particulate Nitrate

Figure 2-6 depicts 1999 annual mean concentrations of nitrate aerosols. The concentrations show considerable intersite variability among nearby sites. For example, sites in Pennsylvania observed concentrations that varied by factors of 1.0 to 2.5 to 4.0. A region from Illinois through Indiana, northern Ohio, Michigan and into Ontario experienced annual mean concentrations above 2.0 $\mu\text{g}/\text{m}^3$.

Total Nitrate

Total nitrate ($\text{HNO}_3 + \text{NO}_3^-$) concentrations for 1999 are shown in Figure 2-7. The pattern is similar to the distribution of HNO_3 .

Particulate Ammonium

Figure 2-8 presents annual mean concentrations of NH_4^+ for 1999. Concentrations peak in the Midwest and South and are fairly uniform

geographically, with observed downward gradients from Pennsylvania across New England and from Illinois to Minnesota.

Ten-Year Trends

Sulfur Species

One of the major goals of CASTNet is to monitor trends in air quality and deposition. Figure 2-9 presents a map of the locations of the 34 eastern and 6 western sites used to perform trends analyses using linear regressions of pollutant concentrations averaged over the respective site subsets from 1990 through 1999. Linear regressions were selected for presentation purposes and to demonstrate the nature of the change, i.e., downward or flat. The use of linear regressions does not imply an expected linear relationship of the 34-site or 6-site composite concentrations with time. SO_2 and NO_x emissions summed over the set of eastern states are also shown on the trend diagrams – SO_2 for trends in sulfur species and NO_x for trends in nitrogen species. Box plots of annual average concentrations for the ten-year period have also been prepared. The 34 eastern sites shown in Figure 2-9 were selected using criteria similar to those used by EPA (2000) in their annual air quality trend report. Sites with complete data for 8 of the 10 years were selected. Missing quarterly data were interpolated from adjacent quarterly data, e.g., first quarter 1996 data were interpolated from 1995 and 1997 first quarter data. Missing quarterly means for 1990 or 1999 were assumed equal to adjacent quarterly values. A valid quarterly mean was based on eight valid weeks. Annual means were based on data from four quarters. Trends for the 6 western sites shown in Figure 2-9 were also based on sites that met the completeness criteria.

Figure 2-10 shows linear regressions based on annual and quarterly mean SO_2 concentrations aggregated over the 34-station subset. Annual SO_2 emissions for states east of and including the north-south line of states from Minnesota to Louisiana are also depicted. P-values are shown on each regression plot. The p-value is defined as the probability that the slope of the straight line fit through the data is zero. A p-value of less than 0.05 is considered statistically significant. The figure shows significant reductions in annual and quarterly SO_2 averages. The data indicate a close relationship between changes in aggregated concentrations and aggregated emissions. Changes in quarterly means are more pronounced in the two colder quarters when SO_2 emissions are higher and there is little photochemical conversion of SO_2 to SO_4^{2-} .

Figure 2-11 presents trends in the 34-station annual data through a box diagram. The inter-site variability among the 34 sites is shown graphically by the 90th percentile, 75th percentile, median, 25th percentile, and 10th percentile values for the annual averages. Aggregated SO_2 emissions data are also plotted as diamonds. The box plot results are similar to the linear regressions.

The trends for the western sites were prepared and analyzed similarly to the eastern sites, except that only six sites (Figure 2-9) met completeness criteria. Figure 2-12 presents a linear trend analysis for the

six western sites. The sum of annual SO_2 emissions for states west of and including the north-south line of states from North Dakota to Texas are also depicted. The regression line shows a small decline in annual SO_2 concentrations.

To provide perspective to the distribution of SO_2 concentrations and to the changes in annual mean concentrations, Figure 2-13 provides information by state on changes in emissions in tons over the period 1990 through 1999. Six different colors illustrate the state-by-state changes in emissions. Also included in the figure are circles that illustrate the changes (in $\mu\text{g}/\text{m}^3$) in concentrations over the ten years. The circles characterize the magnitude of reductions in SO_2 concentrations at CASTNet sites. The legend in the figure provides a scale that can be used to gauge the concentration changes. For example, the largest circle indicates a reduction of $8.0 \mu\text{g}/\text{m}^3$. The reductions in concentrations at individual sites can be compared to changes in SO_2 emissions in nearby states.

Trends in annual and quarterly SO_4^{2-} concentrations are shown in Figure 2-14. Annual SO_2 emissions are also plotted. The data show a reduction in the 34-station annual sulfate concentrations over the 10 years. Second and third quarter levels show the largest decreases. A box plot of annual SO_4^{2-} concentrations is given in Figure 2-15. A trend analysis for sulfate measured at the six western sites is given in Figure 2-16. The data indicate no trend over the 10 years for the six western sites.

Figure 2-17 illustrates changes by state in SO_2 emissions and also in mean sulfate concentrations. Six colors show the magnitude of the emission changes while circles present information on the changes in concentrations over the ten years. The largest circle signifies a reduction of $2.5 \mu\text{g}/\text{m}^3$.

Because sulfate has declined less rapidly than SO_2 , an analysis of the relative contribution of sulfate to atmospheric sulfur loading was performed. Figure 2-18 presents a box plot of the ratio of aggregated annual sulfate concentrations (as S) to total sulfur ($\text{SO}_2 + \text{SO}_4^{2-}$, as S). The analysis shows a slight increase in the mean sulfate fraction over the 10 years.

Nitrogen Species

Linear regressions were also performed on annual and quarterly mean HNO_3 concentrations measured over the ten years. The results for the 34-station composite annual and quarterly averages are shown in Figure 2-19. Annual NO_x emissions are also shown. The results show no significant change over the ten-year period. A box plot of trends in annual average HNO_3 concentrations for the 34 eastern sites is given in Figure 2-20. The results for the western sites are shown in Figure 2-21.

Figure 2-22 shows changes by state in NO_x emissions and also in HNO_3 concentrations over the period 1990 through 1999. Six colors illustrate increases and decreases in emissions while circles show changes in

concentrations. Gray circles show reductions and white show increases in HNO_3 concentrations.

Trends in annual and quarterly particulate nitrate concentrations are shown in Figure 2-23. Annual NO_x emissions are also plotted. The results show no significant change. A box plot is provided in Figure 2-24. The western sites are shown in Figure 2-25.

The regression analyses for total nitrate levels from the 34-station database are shown in Figure 2-26. NO_x emissions are also plotted. No trends are evident from the regression plots. A box plot of annual total nitrate concentrations is given in Figure 2-27. The western data are plotted in Figure 2-28. No trend is shown for the six western sites.

Linear regressions for annual and quarterly average NH_4^+ concentrations for the 34-station composite database are shown in Figure 2-29. The data show a slight reduction in annual averages over the ten-year period. The rate of change is slightly higher in the second quarter. A box plot is shown in Figure 2-30. The western annual NH_4^+ data are shown in Figure 2-31. No significant trend is evident.

Because nitrogen emissions and concentrations of nitrogen species have not declined over the ten years, an analysis of the relative contribution of nitrogen and sulfur to atmospheric pollution was performed. Figure 2-32 presents a box plot of the ratio of nitrogen to sulfur (in molar units) from the 34-station database. The box plot shows an increase in the nitrogen fraction over the ten years.

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Figure 2-1. Annual Mean SO₂ Concentrations (µg/m³) for 1999

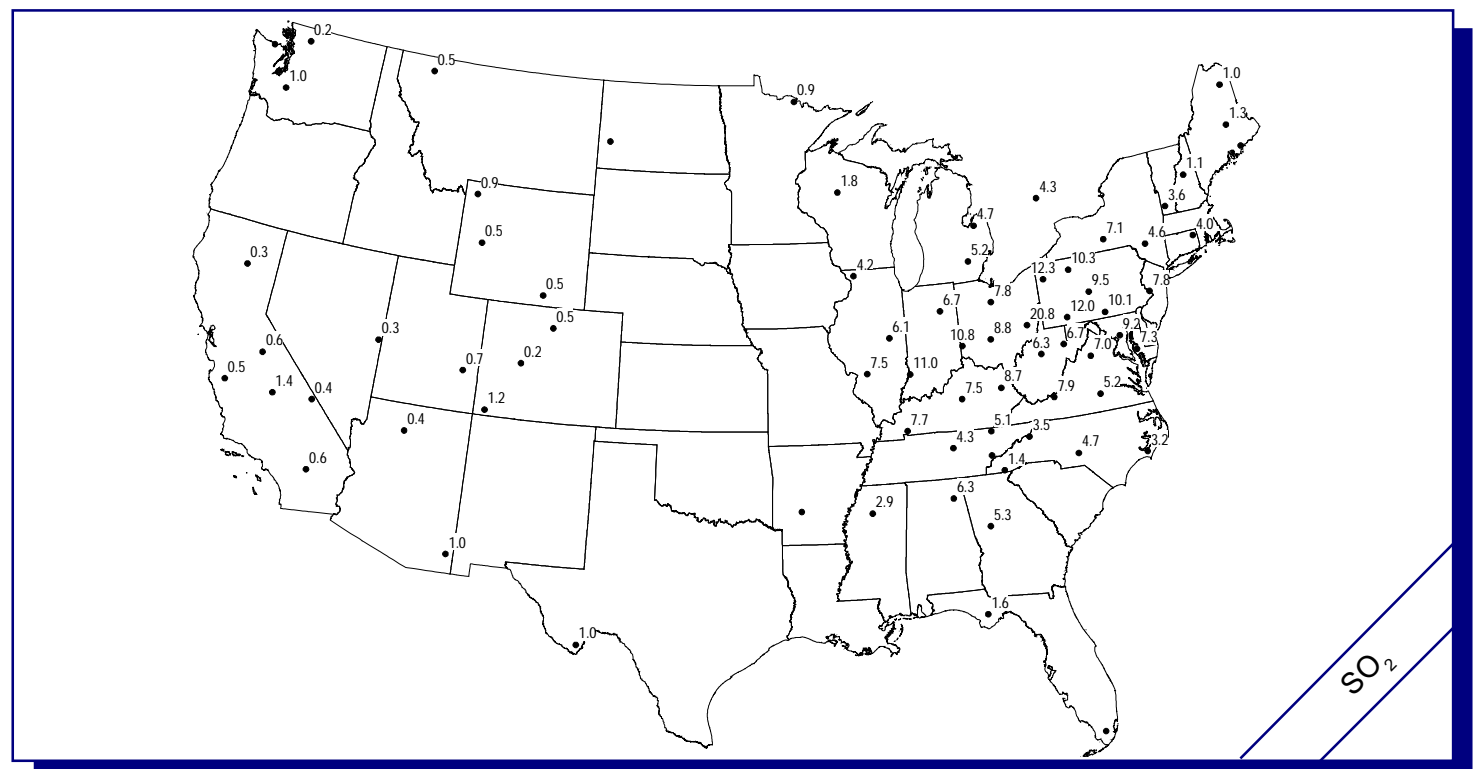


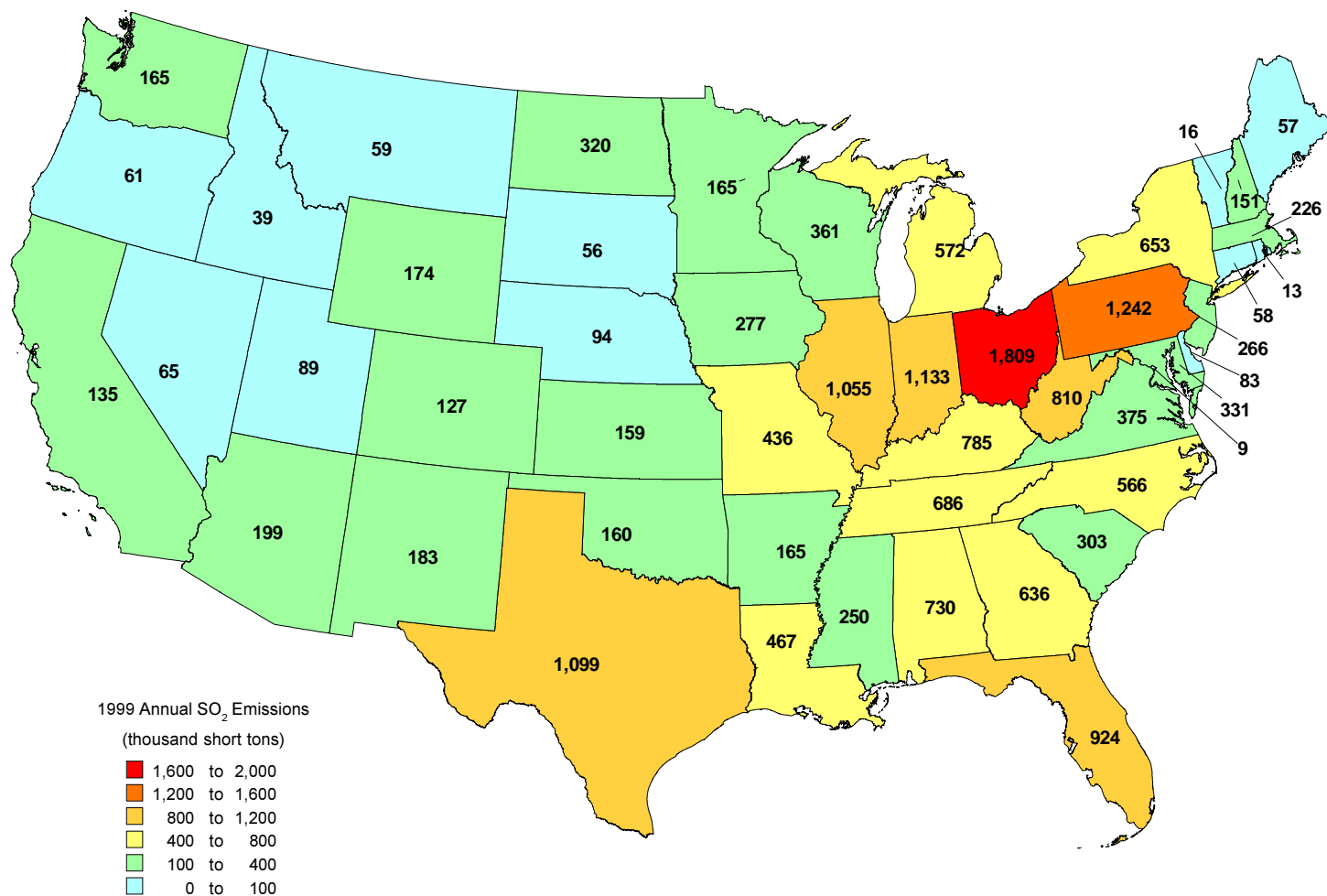
Figure 2-2. Annual SO₂ Emissions (tons) for 1999

Figure 2-3. Annual Mean SO_4^{2-} Concentrations ($\mu\text{g}/\text{m}^3$) for 1999



Figure 2-4. Annual Mean HNO_3 Concentrations ($\mu\text{g}/\text{m}^3$) for 1999



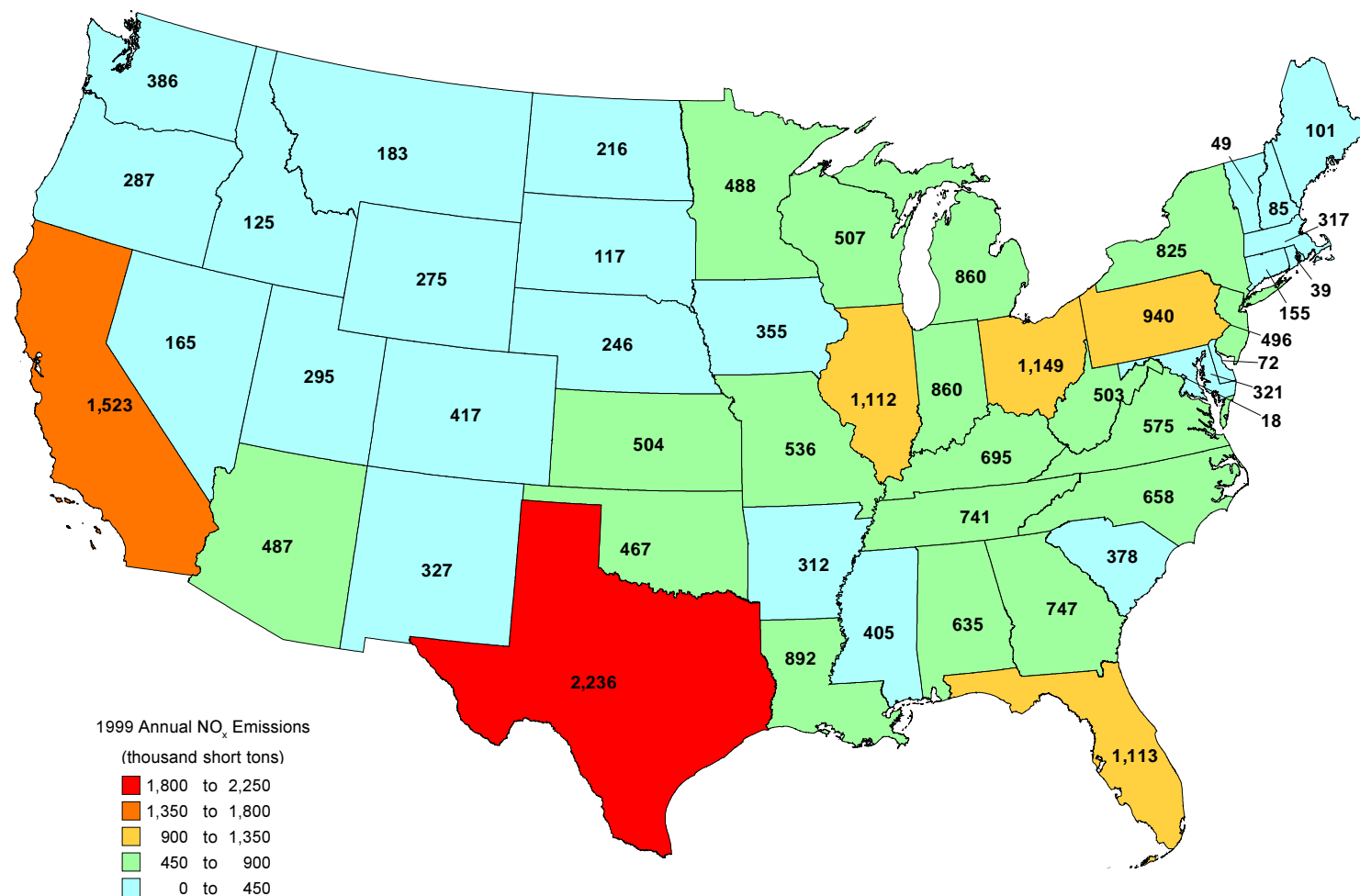
Figure 2-5. Annual NO_x Emissions (tons) for 1999

Figure 2-6. Annual Mean NO₃ Concentrations (µg/m³) for 1999



Figure 2-7. Annual Mean Total NO₃ Concentrations (µg/m³) for 1999

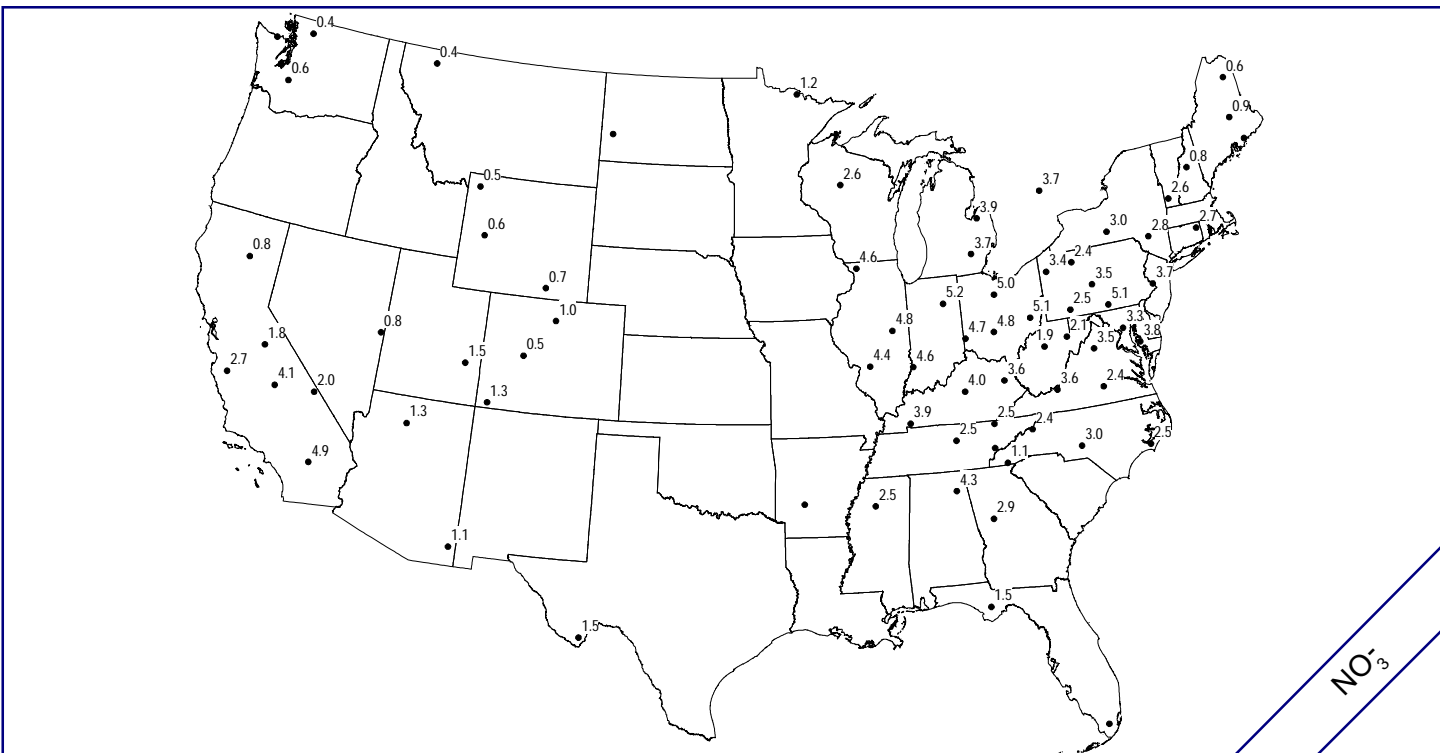


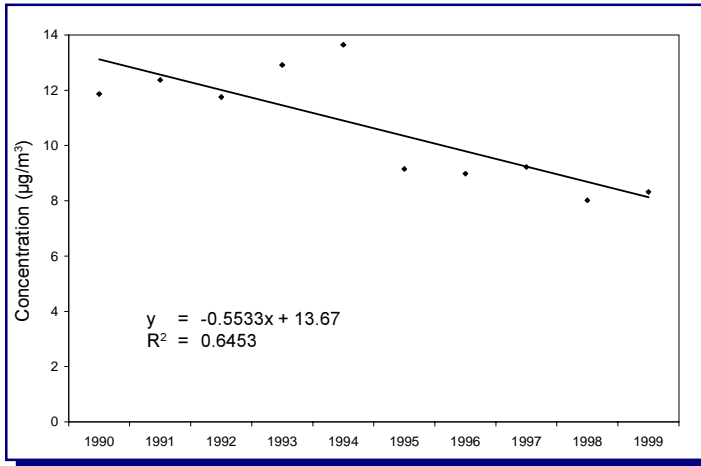
Figure 2-8. Annual Mean NH_4^+ Concentrations ($\mu\text{g}/\text{m}^3$) for 1999



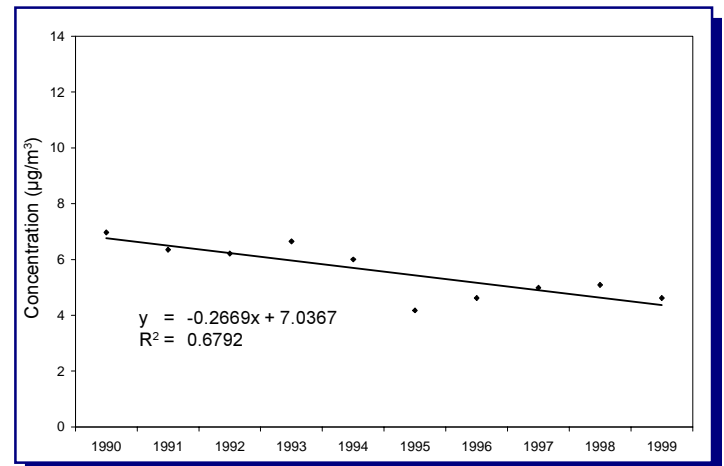
Figure 2-9. Map of 34 Eastern and 6 Western Sites Selected for Trends Analysis



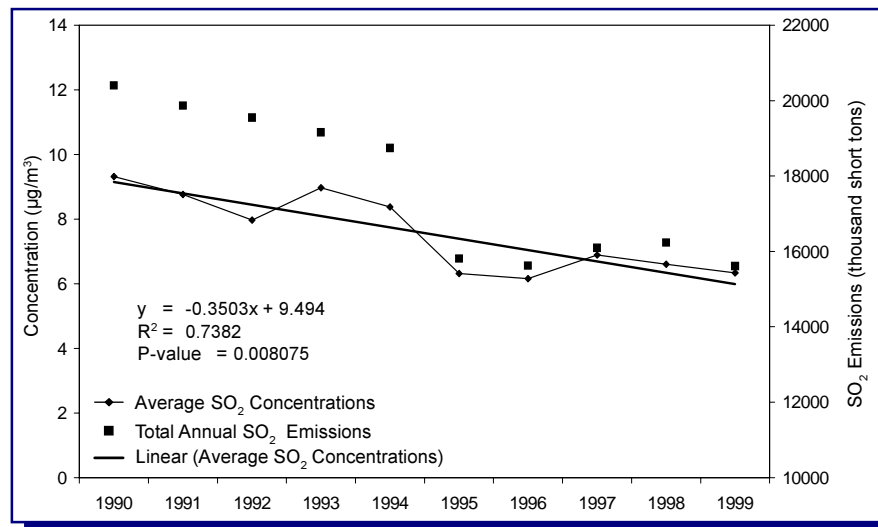
Figure 2-10. Linear Regression Analyses for Annual and Quarterly Average SO₂ Concentrations—Eastern United States



First Quarter

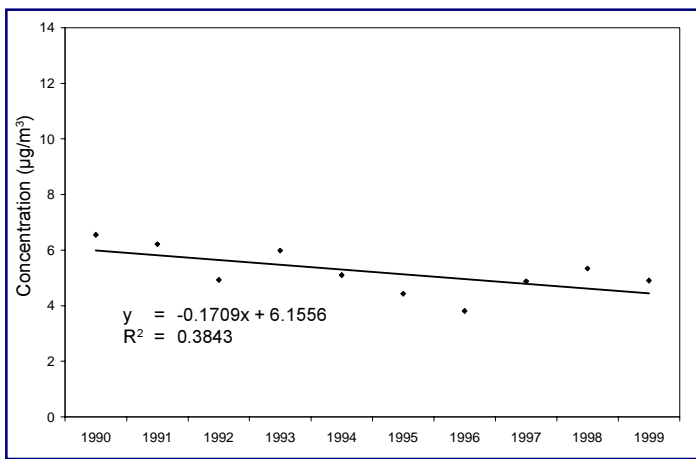


Second Quarter



Annual Average

Third Quarter



Fourth Quarter

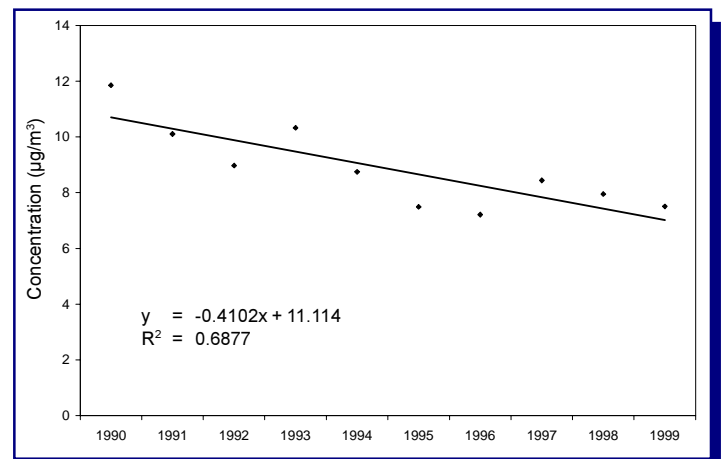


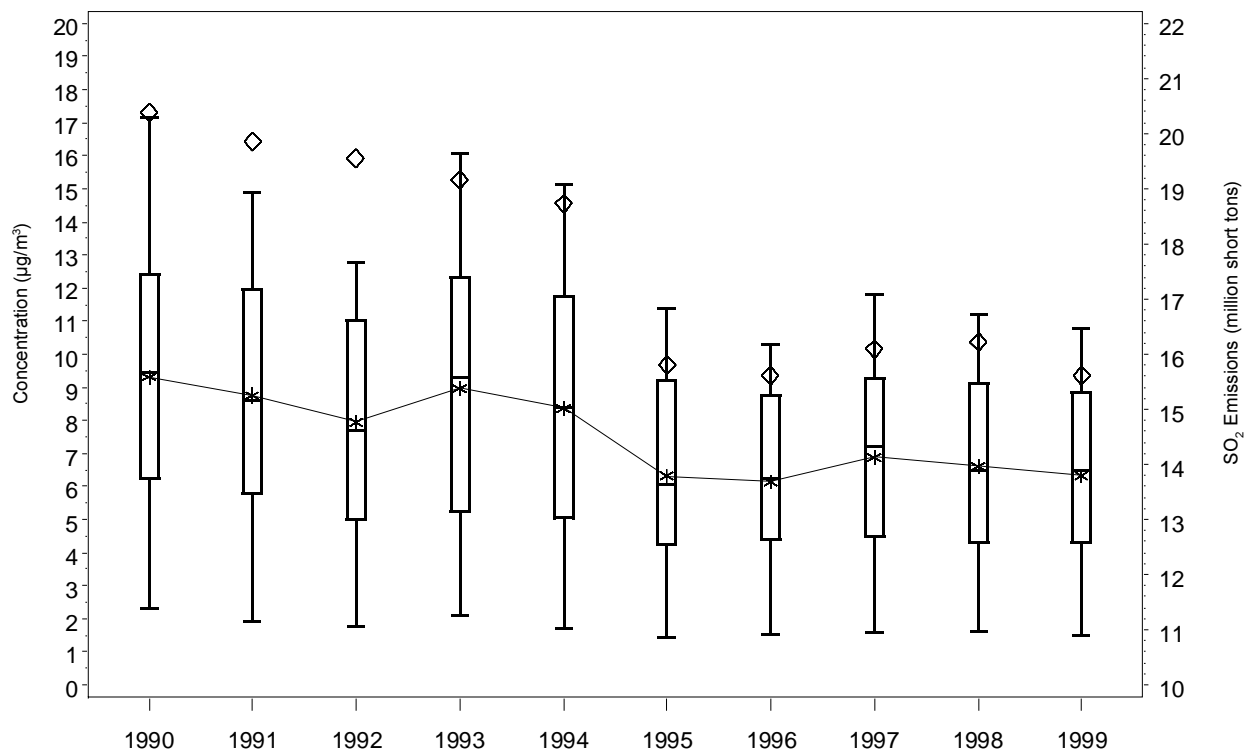
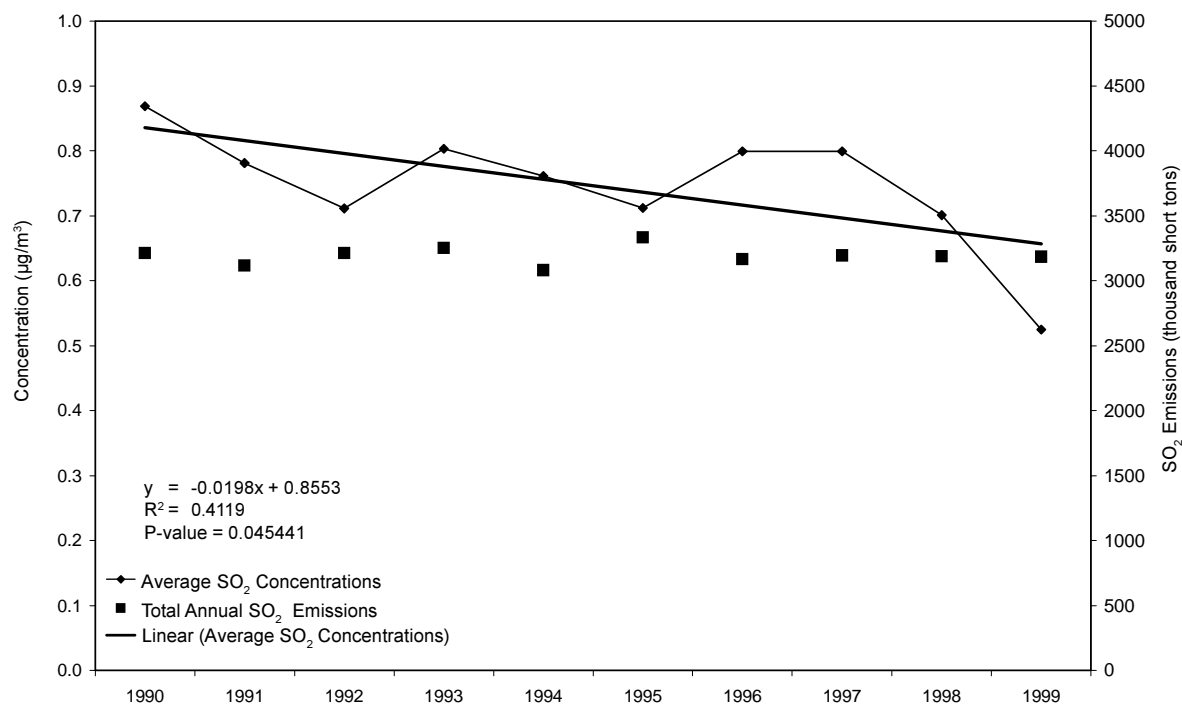
Figure 2-11. Trends in Composite Annual SO₂ Concentrations—Eastern United States**Figure 2-12.** Linear Regression Analyses for Annual Average SO₂ Concentrations—Western United States

Figure 2-13. Differences in Annual Mean SO₂ Concentrations and Changes in Annual SO₂ Emissions from 1990 - 1999

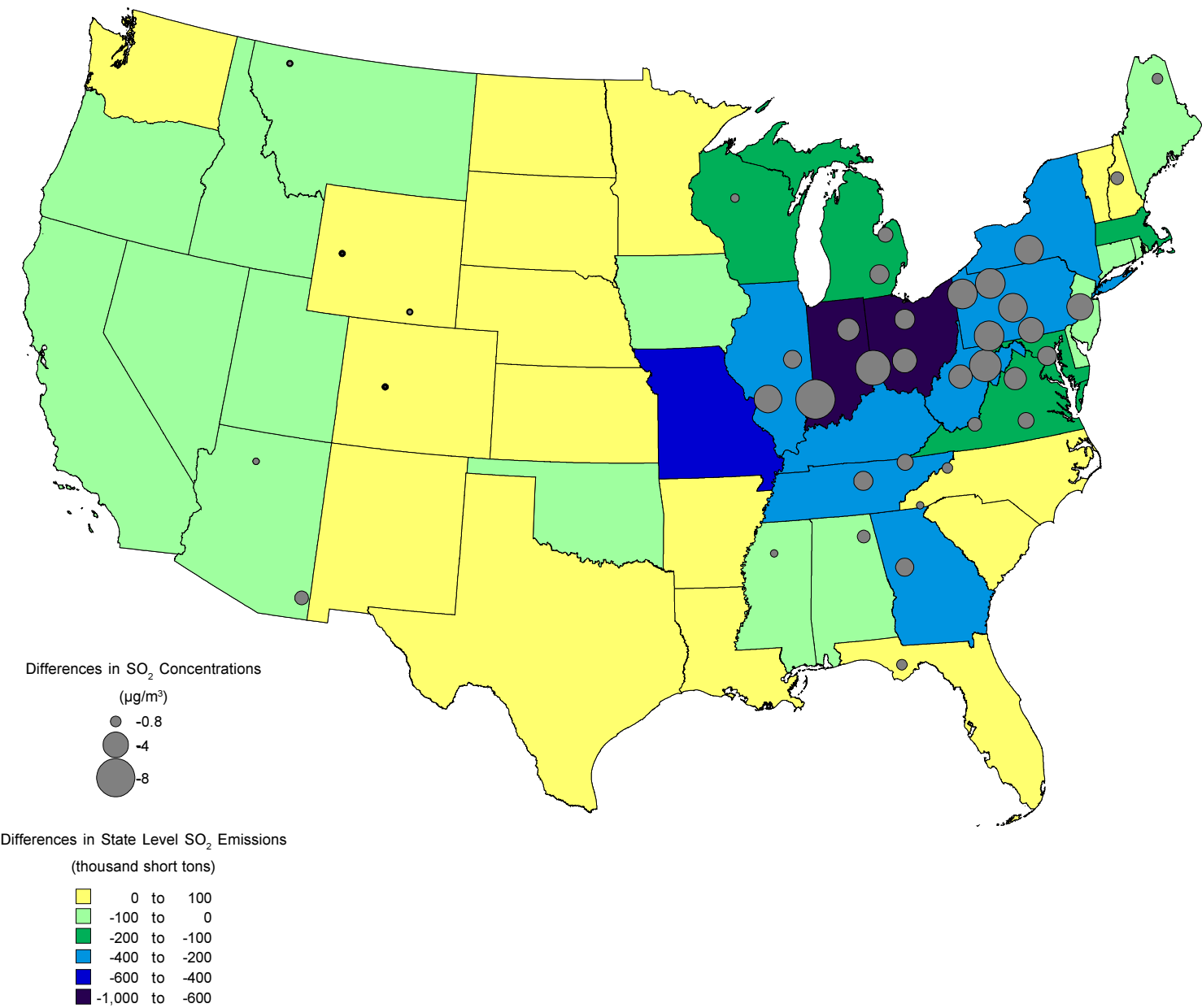
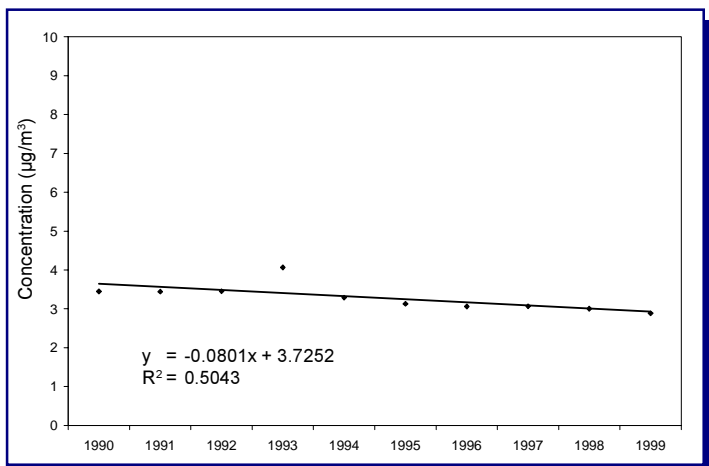
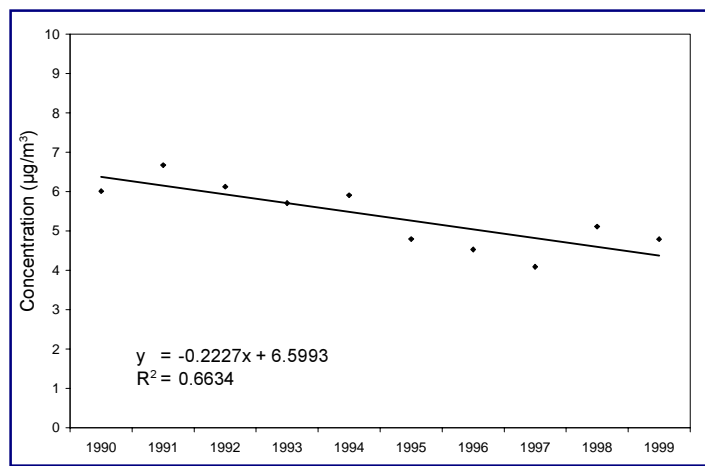


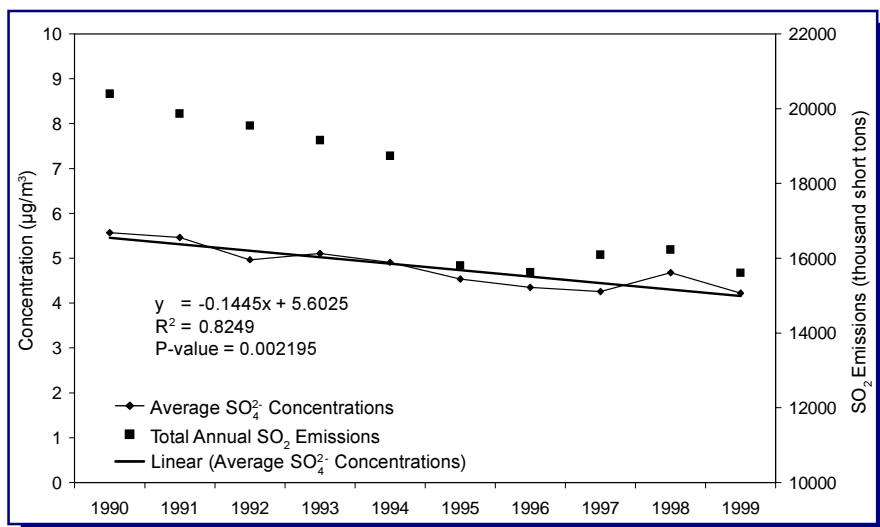
Figure 2-14. Linear Regression Analyses for Annual and Quarterly Average SO_4^{2-} Concentrations—Eastern United States



First Quarter

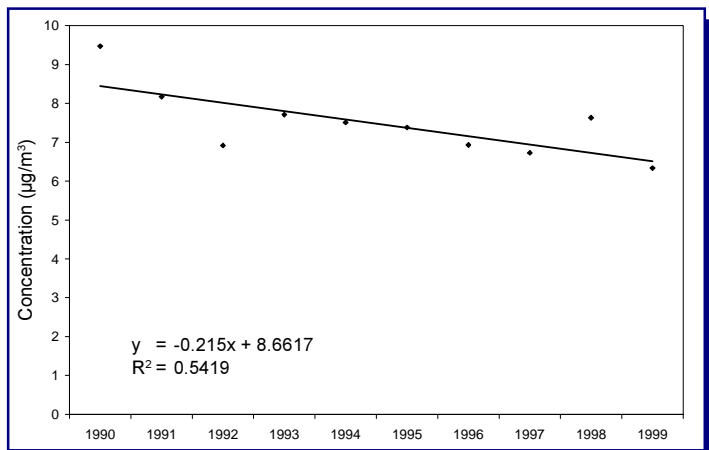


Second Quarter



Annual Average

Third Quarter



Fourth Quarter

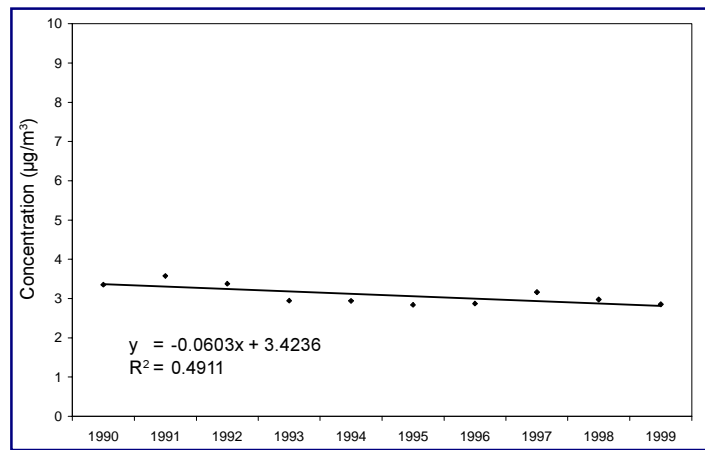


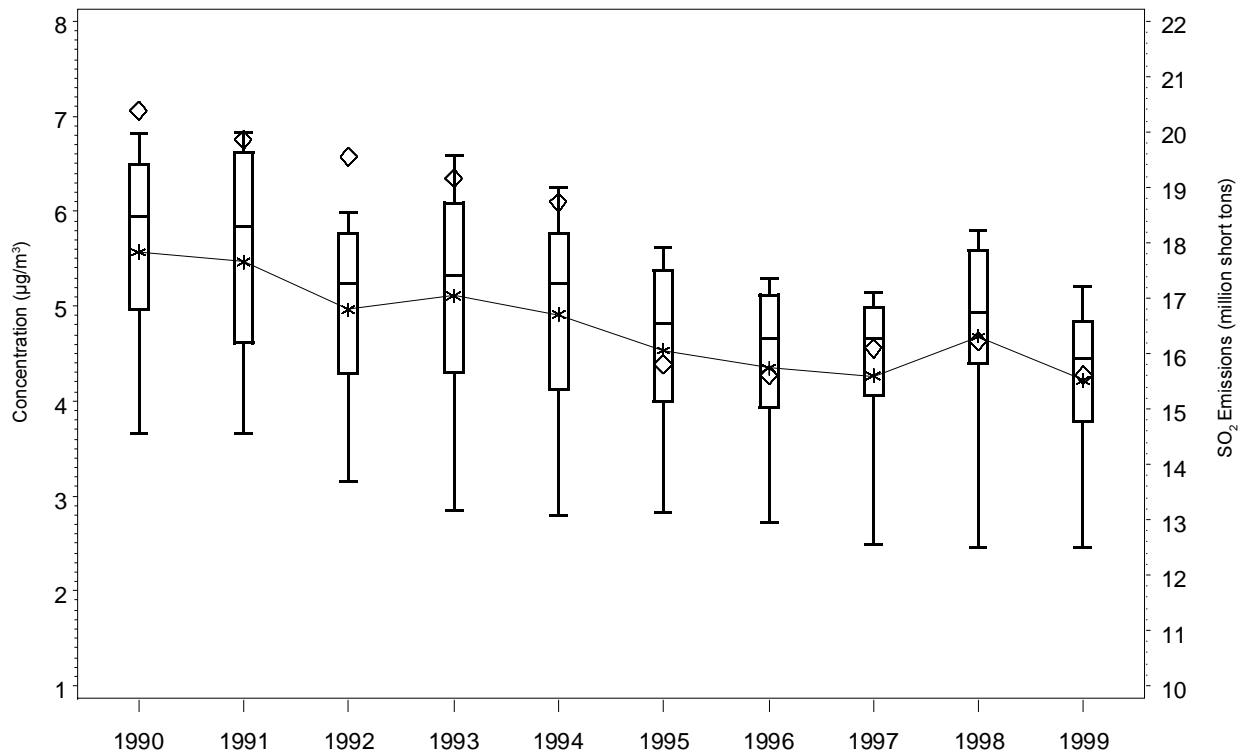
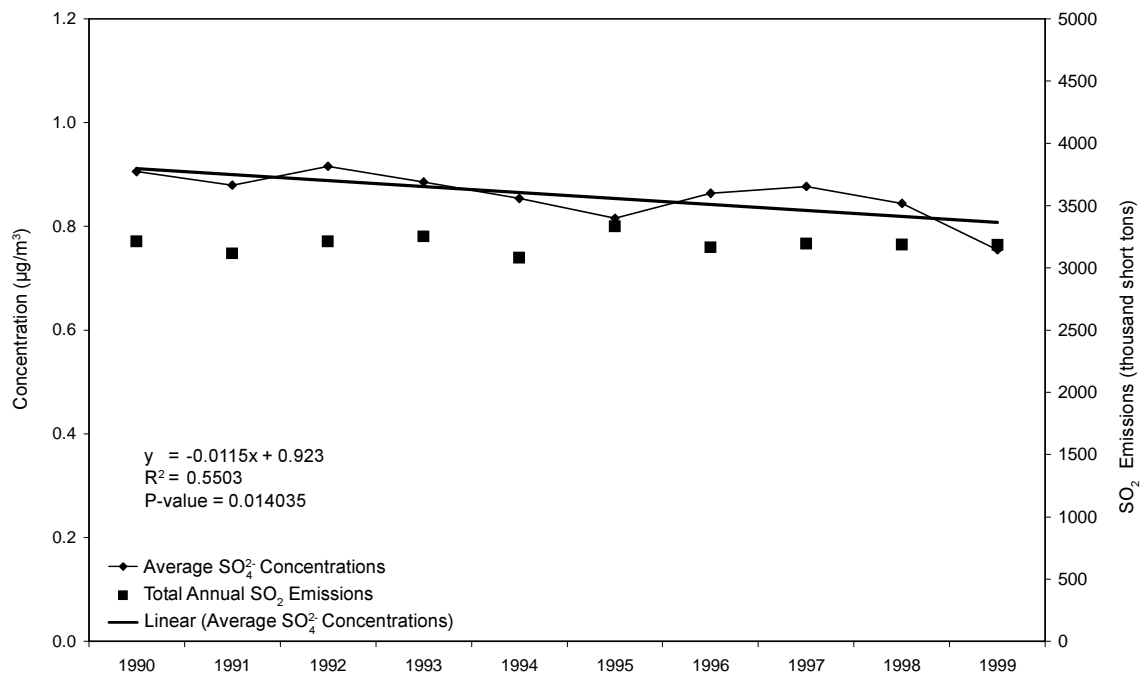
Figure 2-15. Trends in Composite Annual SO_4^{2-} Concentrations—Eastern United States**Figure 2-16.** Linear Regression Analyses for Annual Average SO_4^{2-} Concentrations—Western United States

Figure 2-17. Differences in Annual Mean SO_4^{2-} Concentrations and Changes in Annual SO_2 Emissions from 1990 - 1999

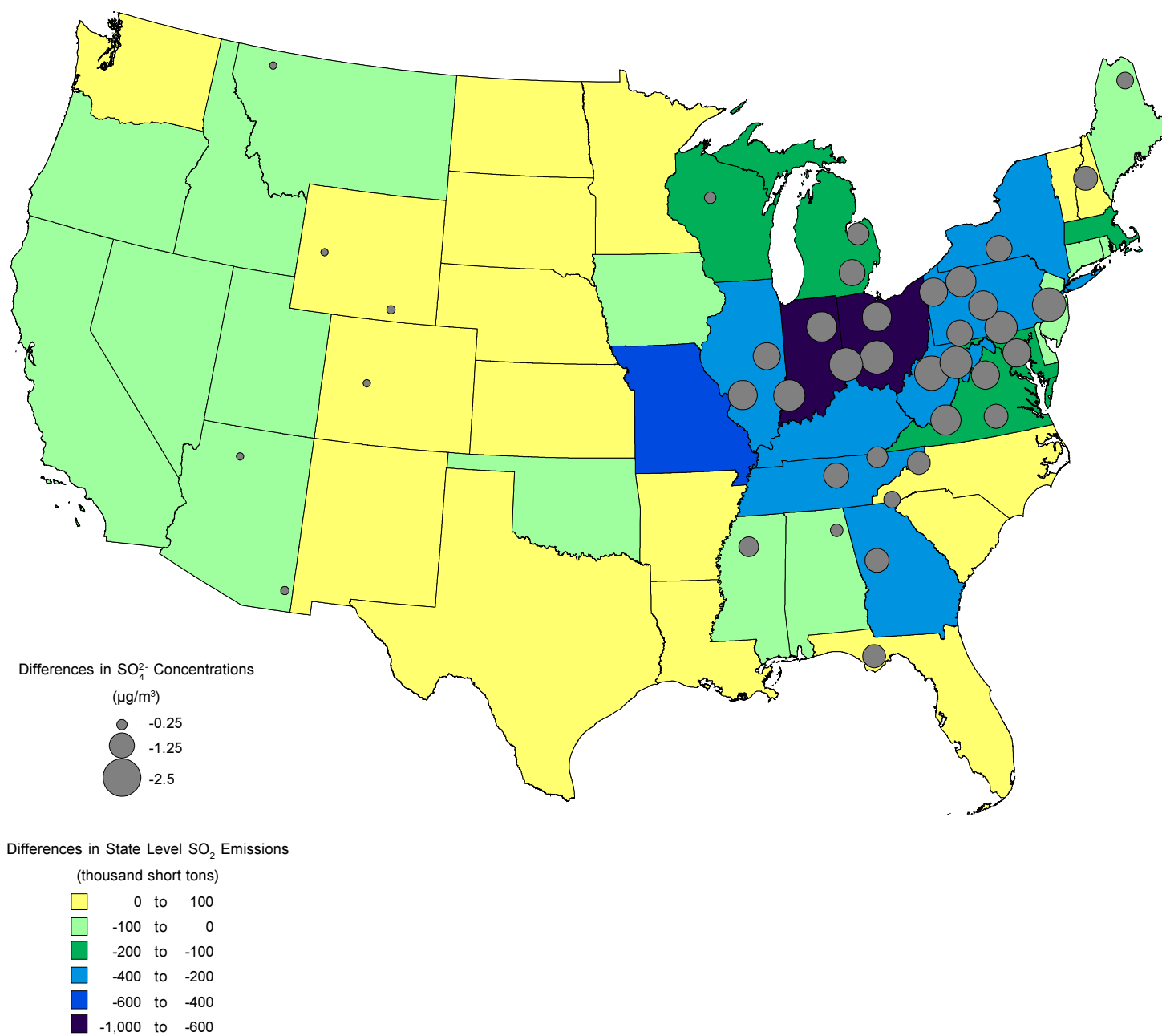


Figure 2-18. Fraction of SO_4^{2-} as S in Total Sulfur ($\text{SO}_4^{2-} + \text{SO}_2$, as S)—Composite Annual Values—Eastern United States

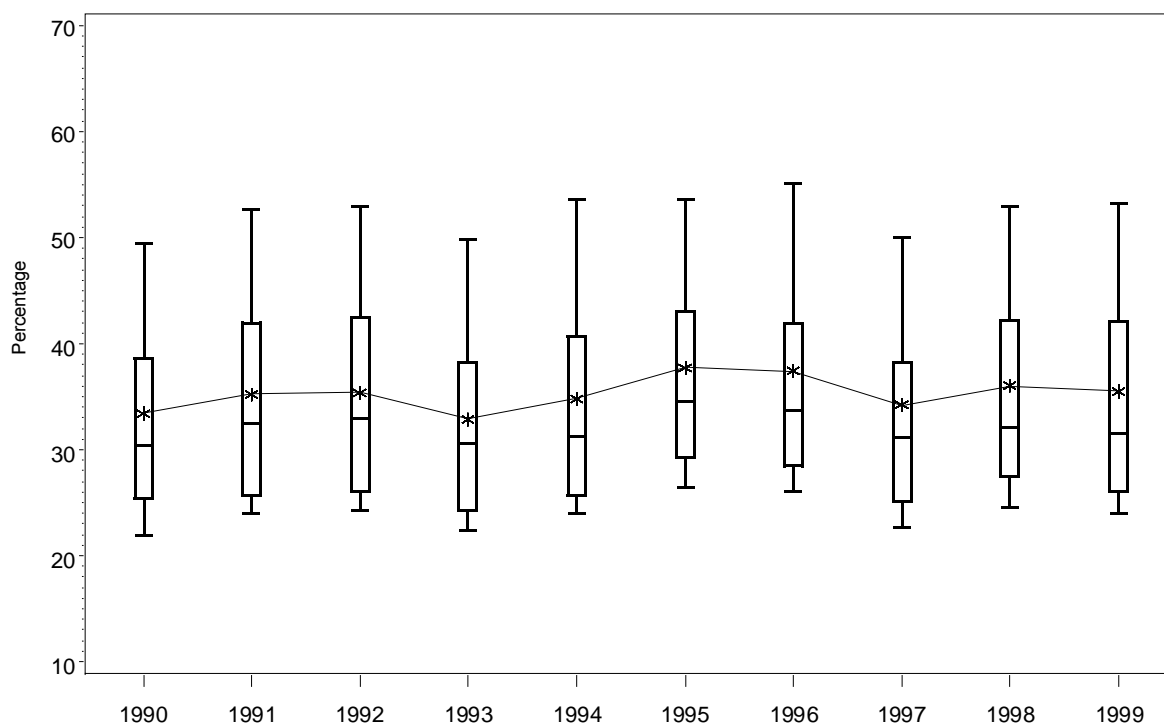
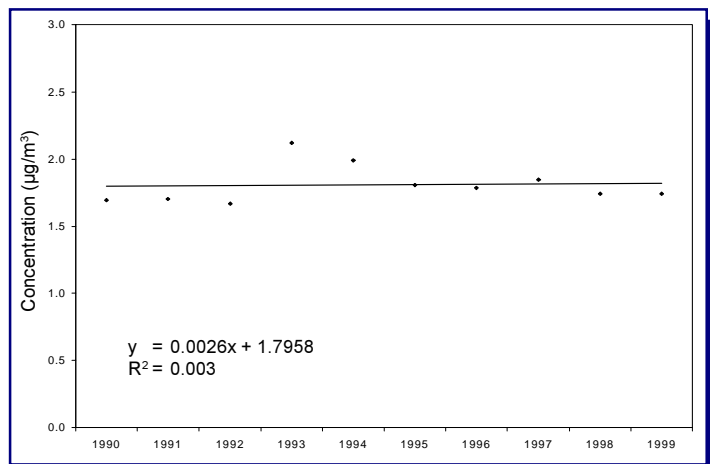
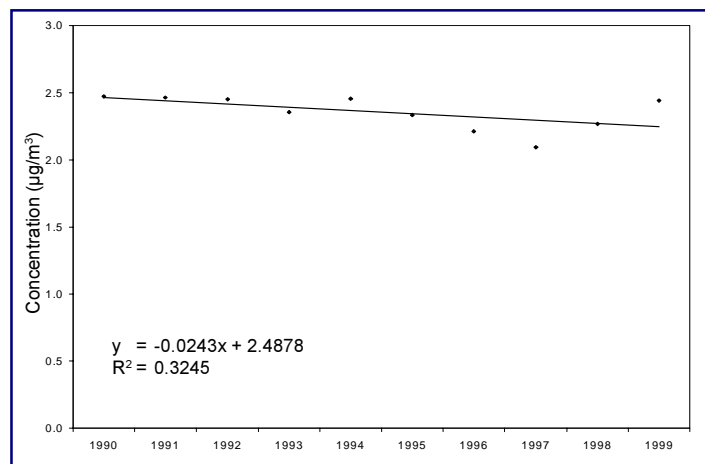


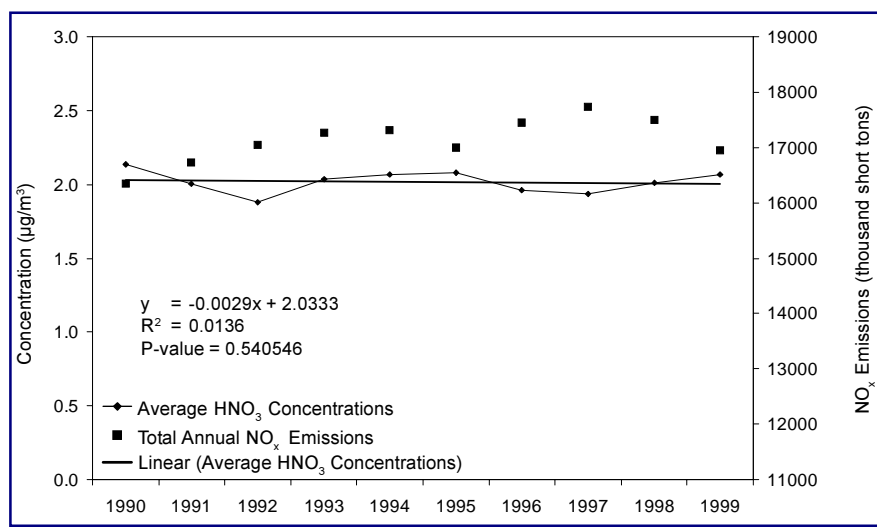
Figure 2-19. Linear Regression Analyses for Annual and Quarterly Average HNO_3 Concentrations—Eastern United States



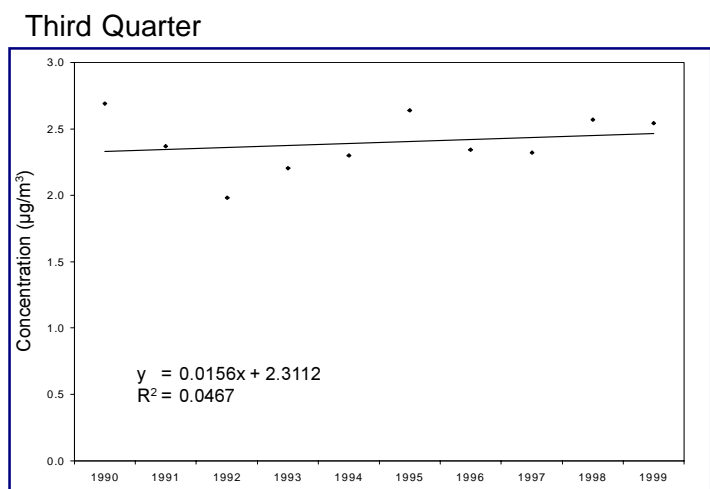
First Quarter



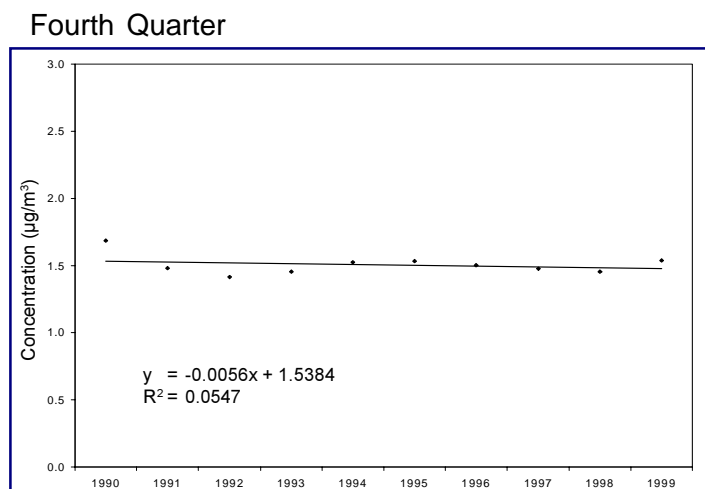
Second Quarter



Annual Average



Third Quarter



Fourth Quarter

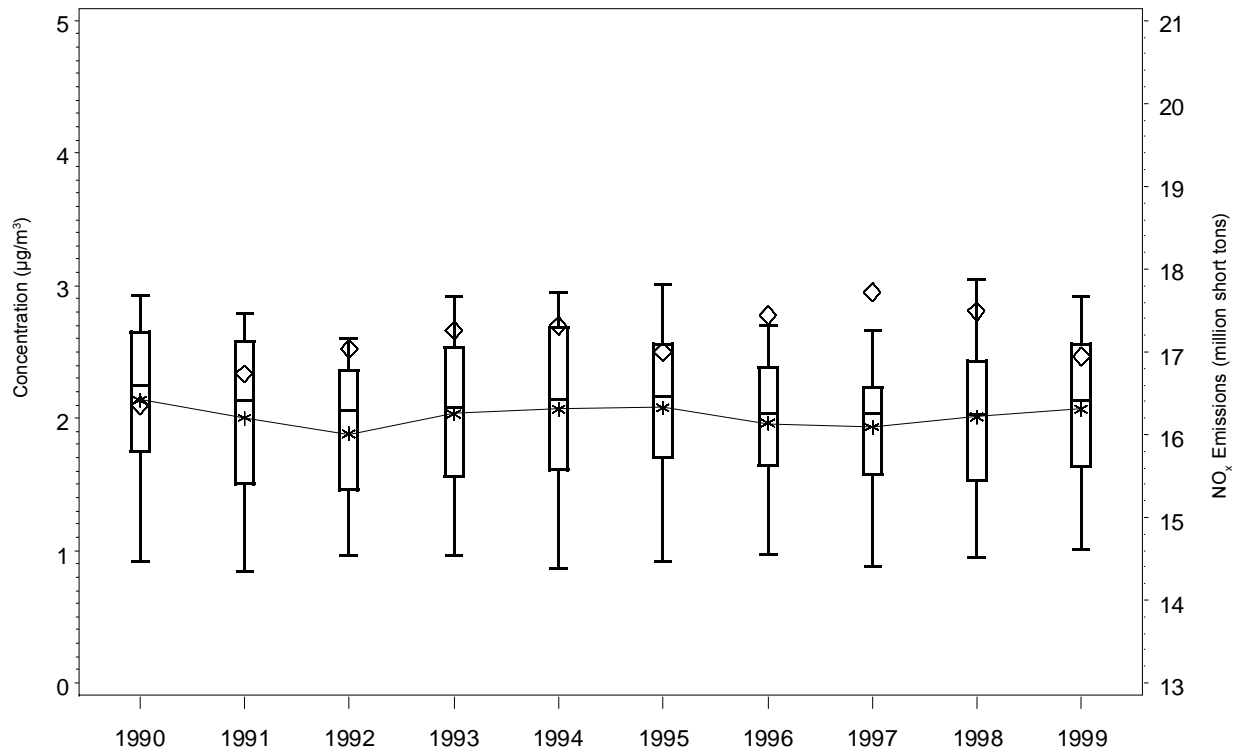
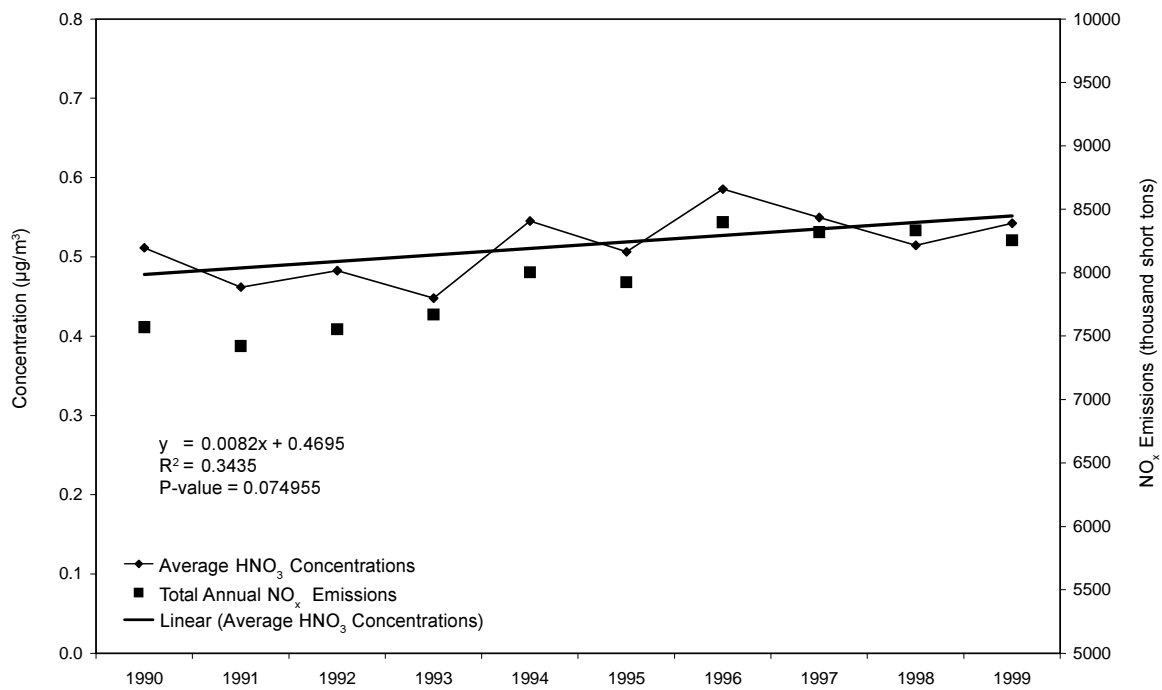
Figure 2-20. Trends in Composite Annual HNO_3 Concentrations—Eastern United States**Figure 2-21.** Linear Regression Analyses for Annual Average HNO_3 Concentrations—Western United States

Figure 2-22. Differences in Annual Mean HNO_3 Concentrations and Changes in Annual NO_x Emissions from 1990 - 1999

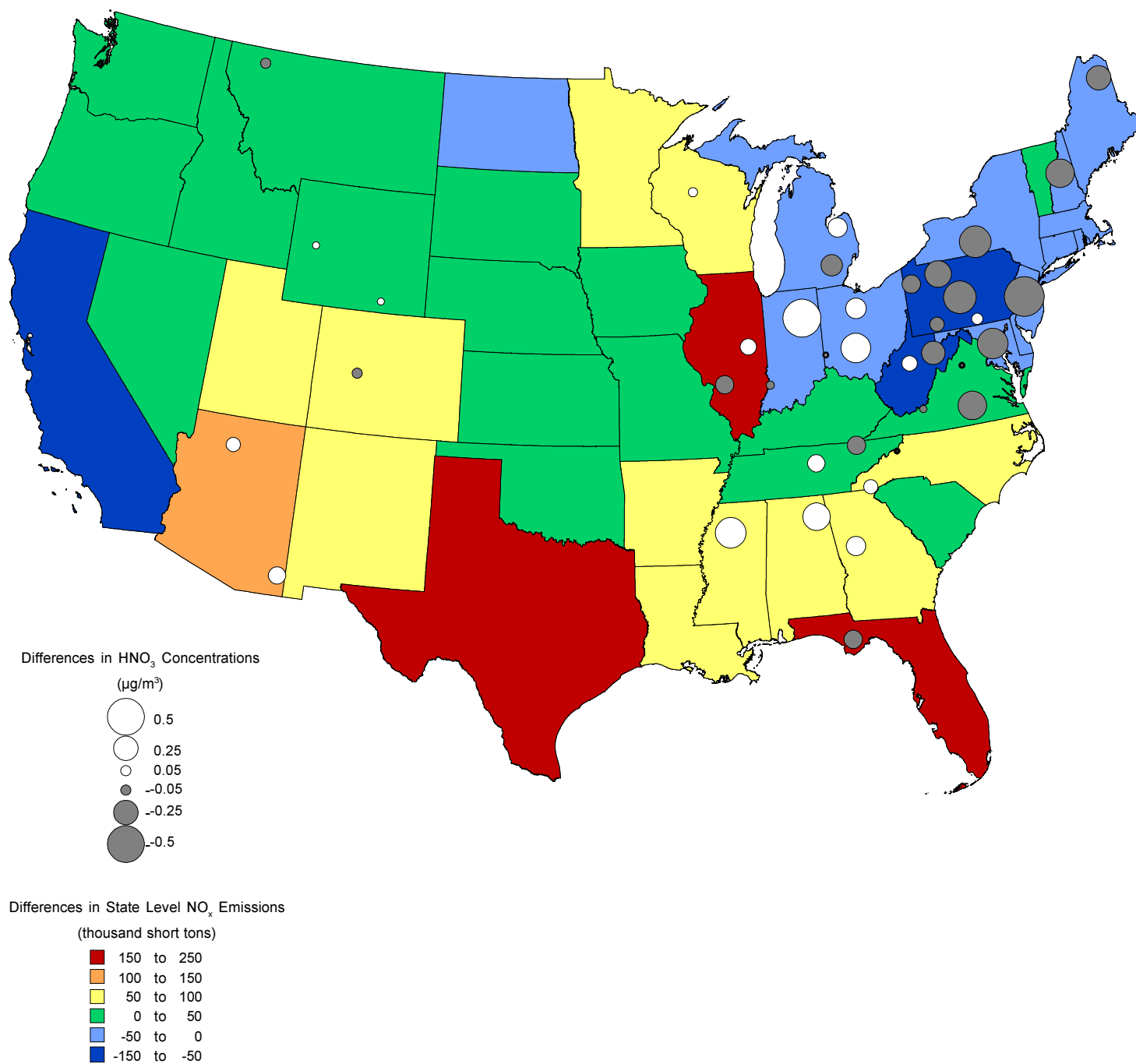
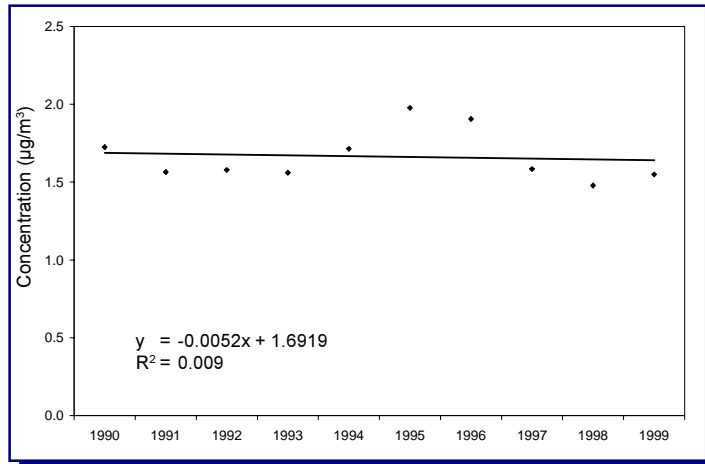
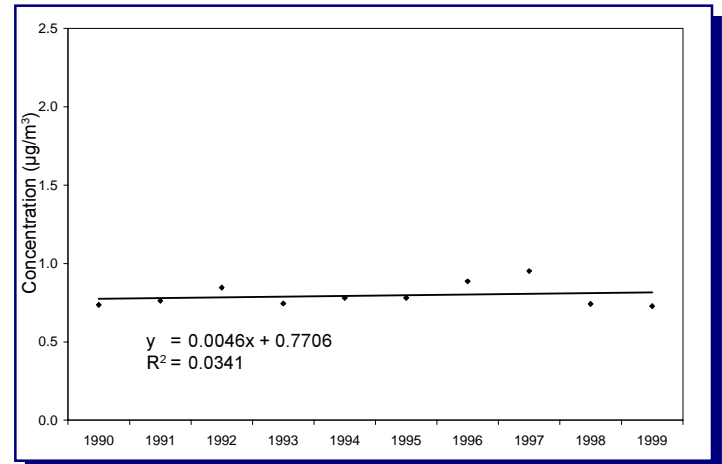


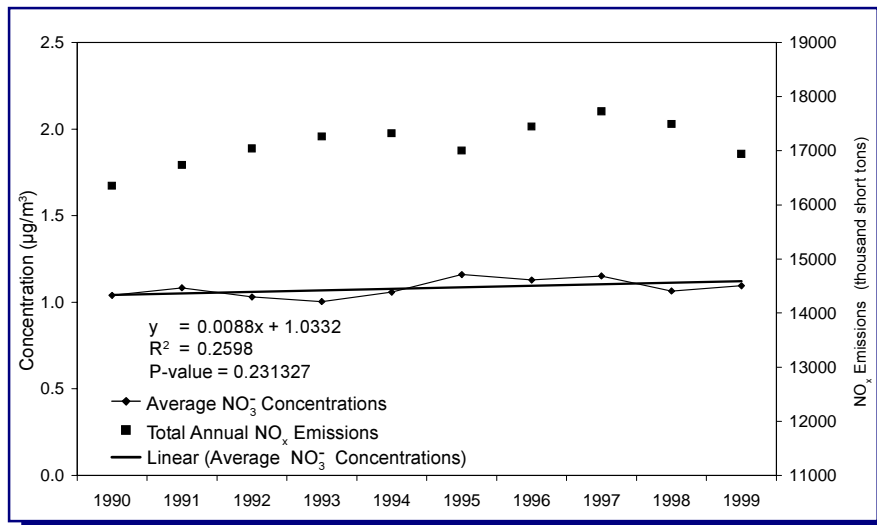
Figure 2-23. Linear Regression Analyses for Annual and Quarterly Average NO_3^- Concentrations—Eastern United States



First Quarter

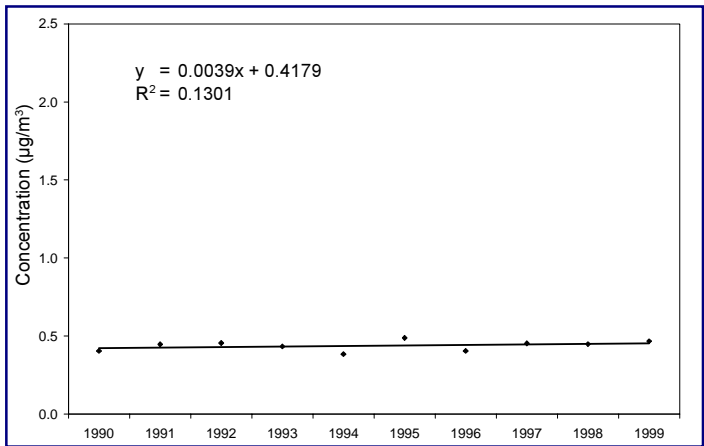


Second Quarter



Annual Average

Third Quarter



Fourth Quarter

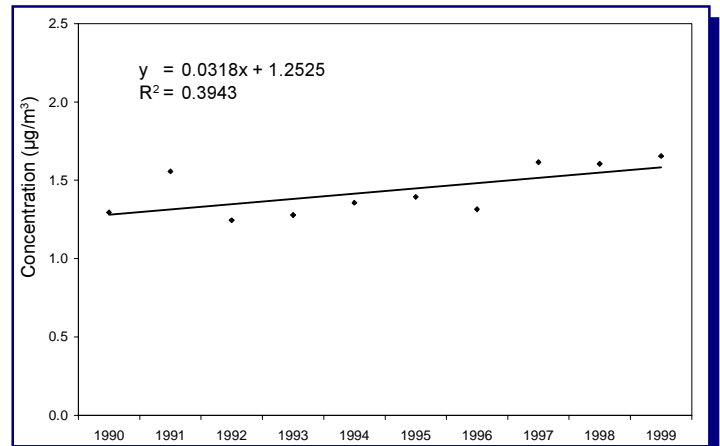


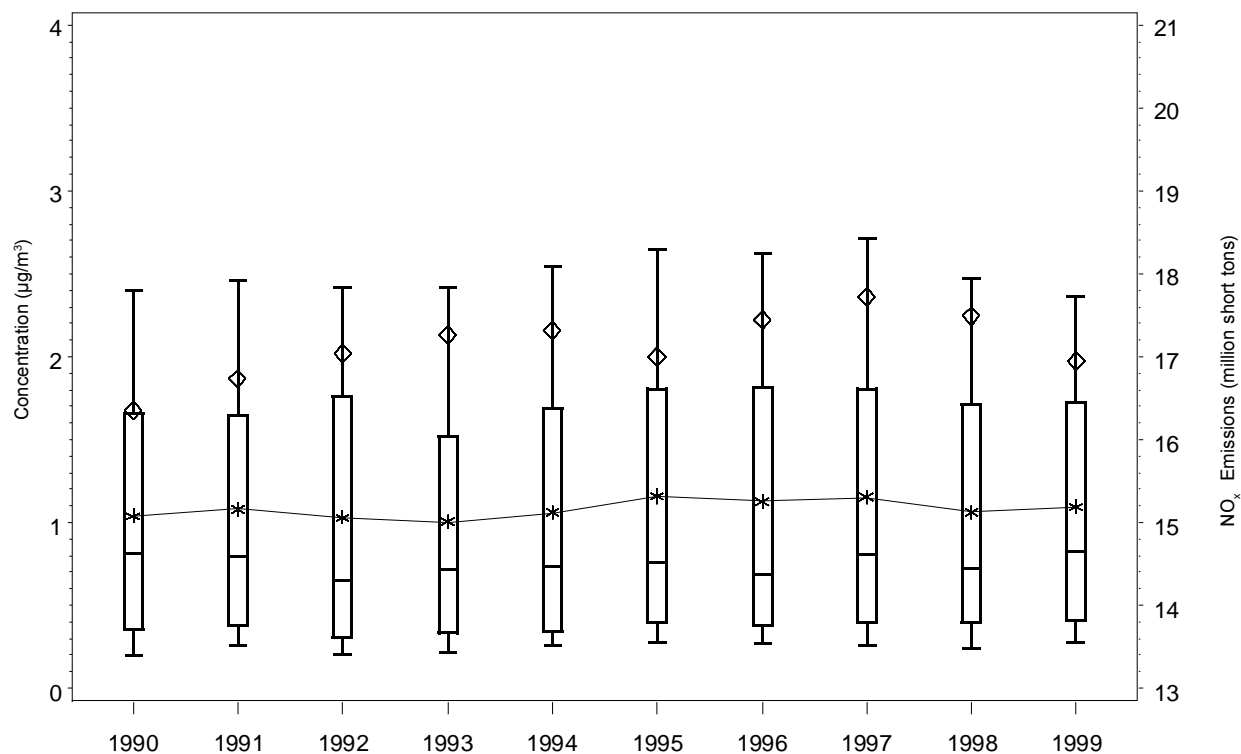
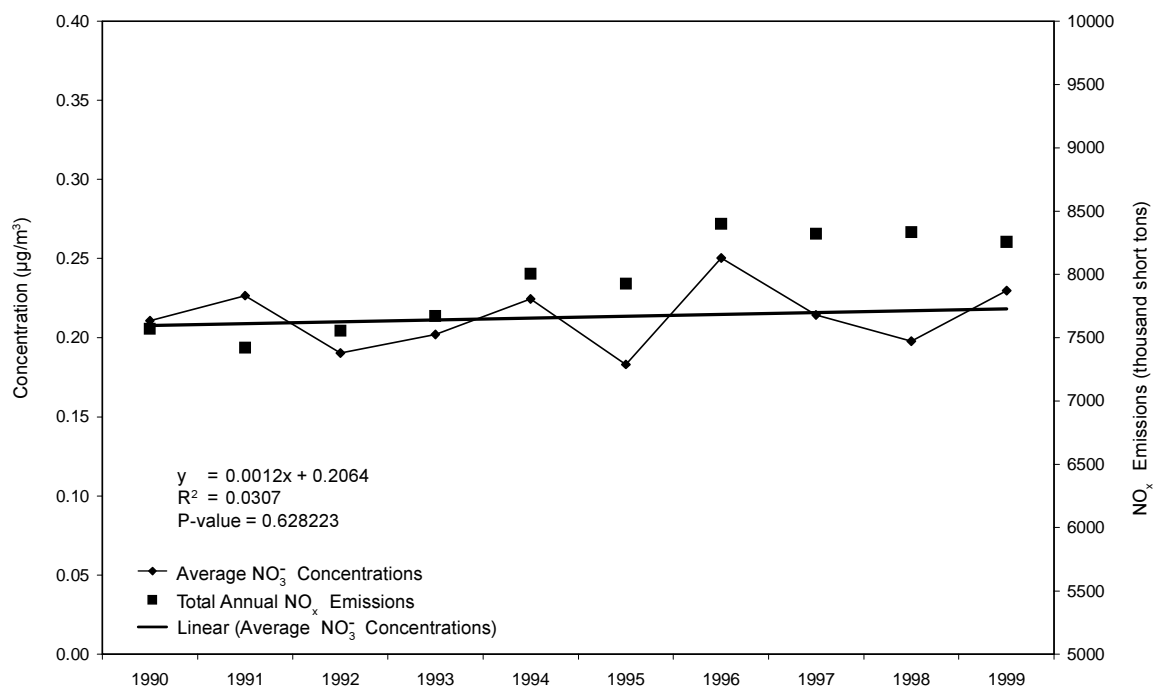
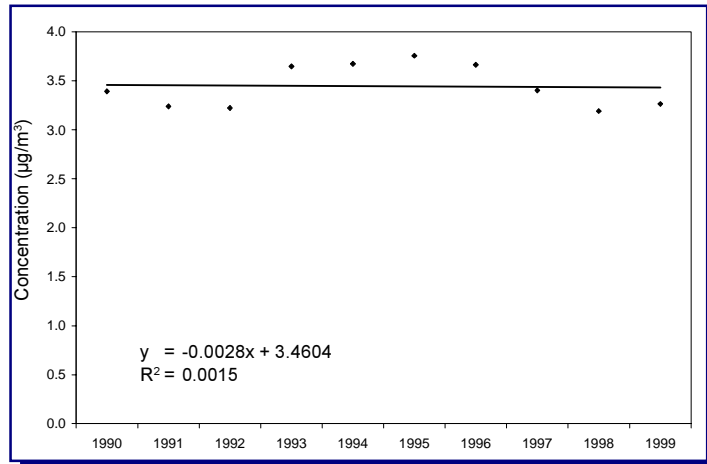
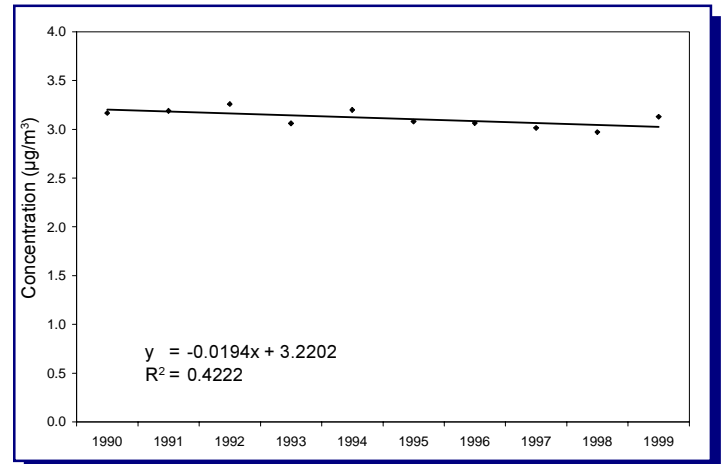
Figure 2-24. Trends in Composite Annual Particulate NO_3^- Concentrations—Eastern United States**Figure 2-25.** Linear Regression Analyses for Annual Average NO_3^- Concentrations—Western United States

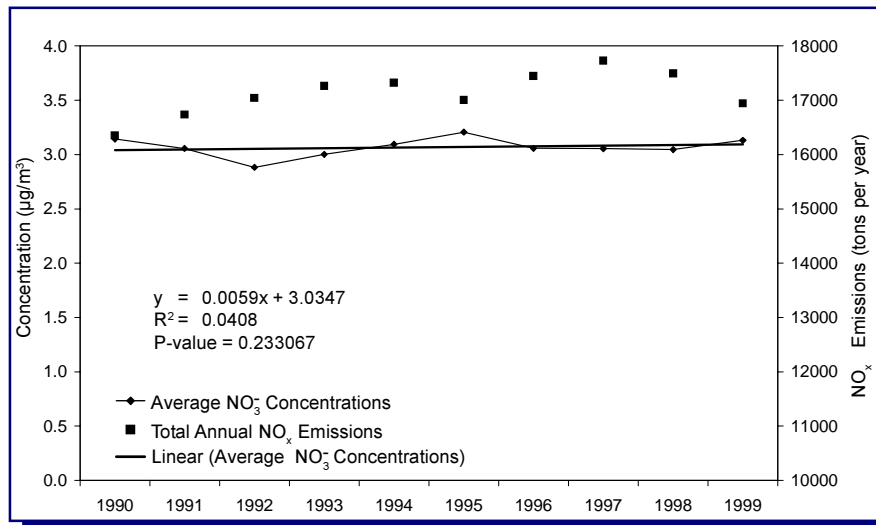
Figure 2-26. Linear Regression Analyses for Annual and Quarterly Average Total NO_3^- Concentrations—Eastern United States



First Quarter

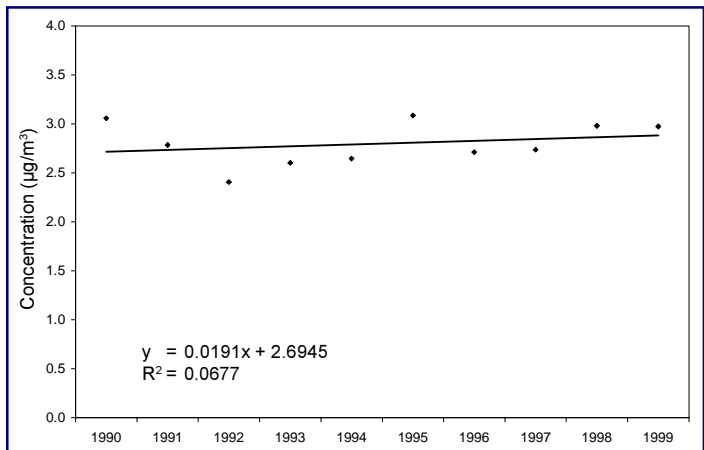


Second Quarter



Annual Average

Third Quarter



Fourth Quarter

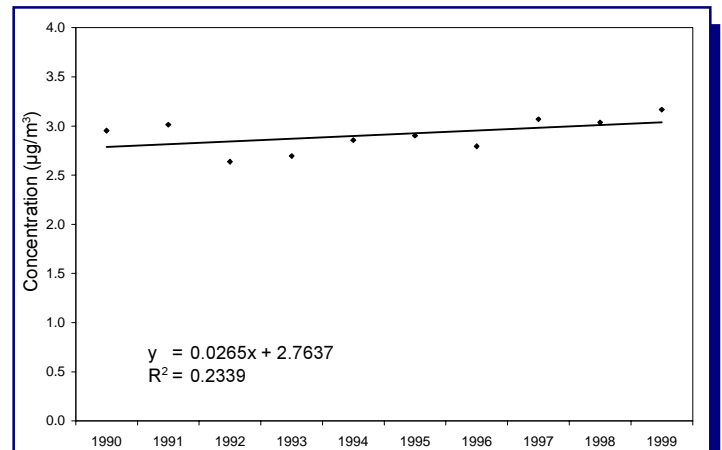


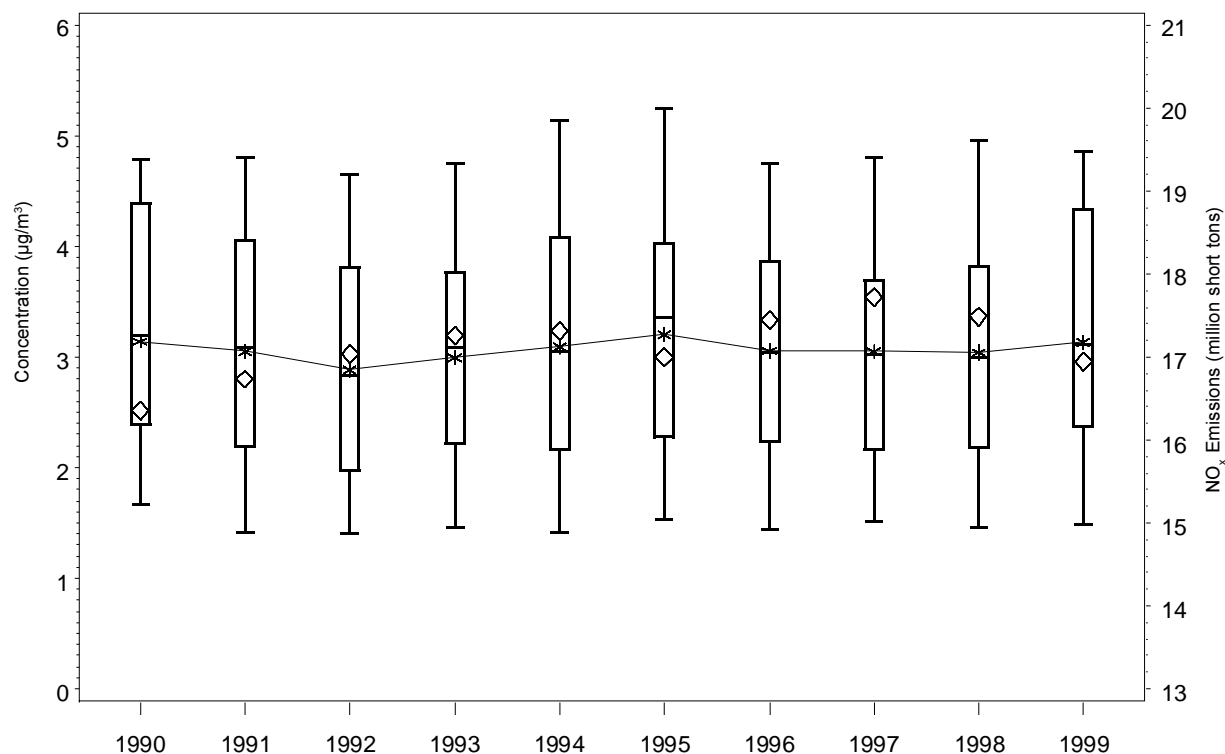
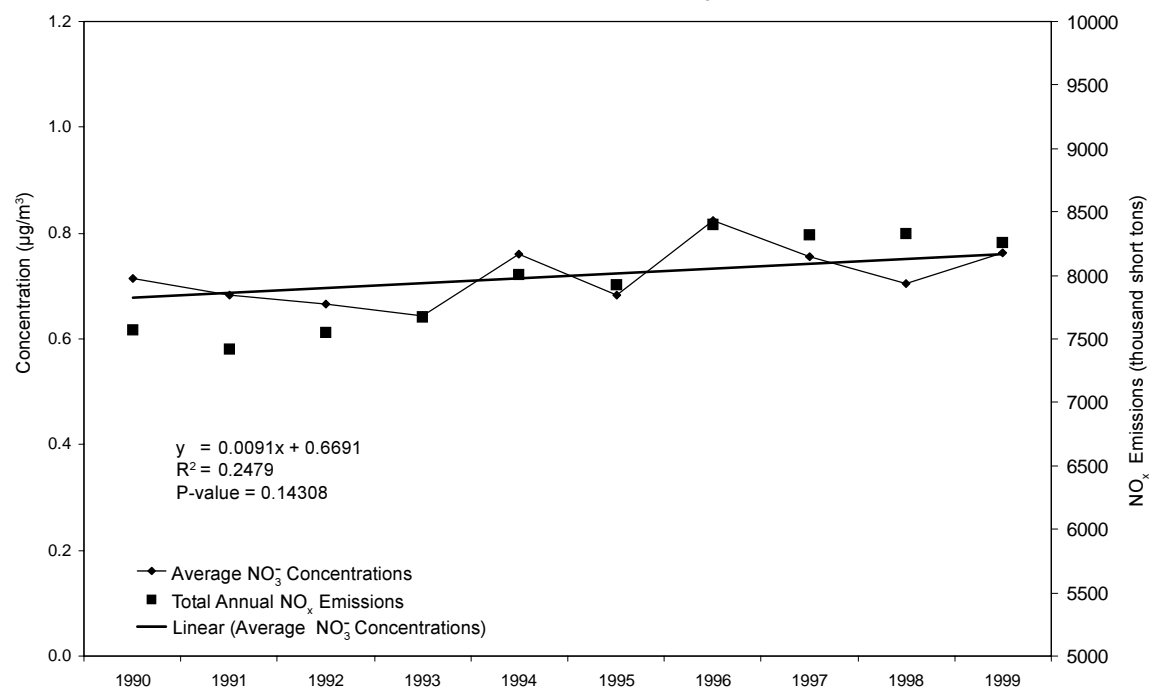
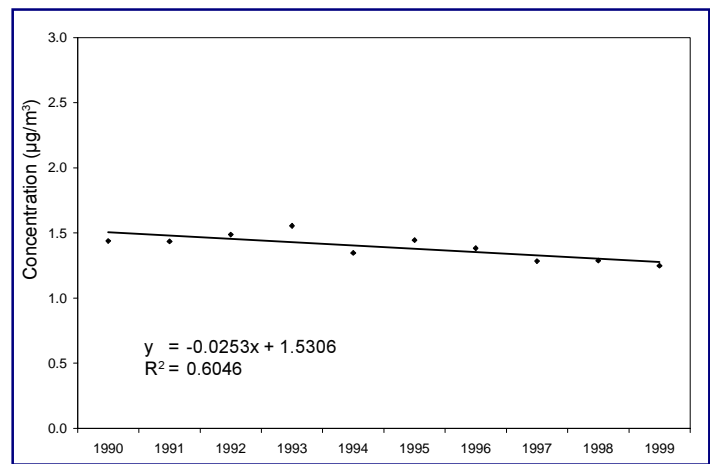
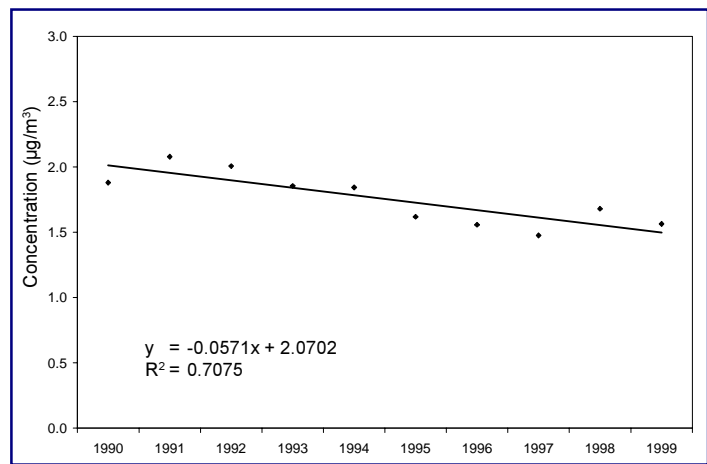
Figure 2-27. Trends in Composite Annual Total NO_3^- Concentrations—Eastern United States**Figure 2-28.** Linear Regression Analyses for Annual Total NO_3^- Concentrations—Western United States

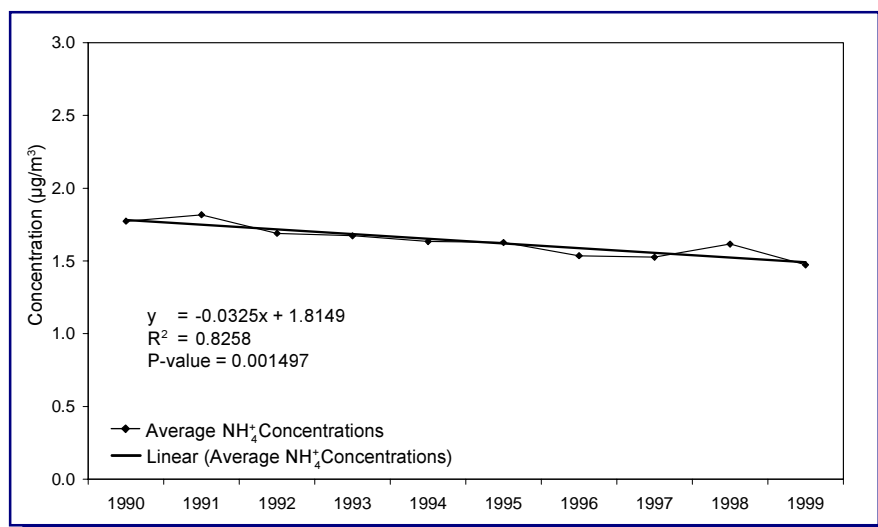
Figure 2-29. Linear Regression Analyses for Annual and Quarterly Average NH_4^+ Concentrations—Eastern United States



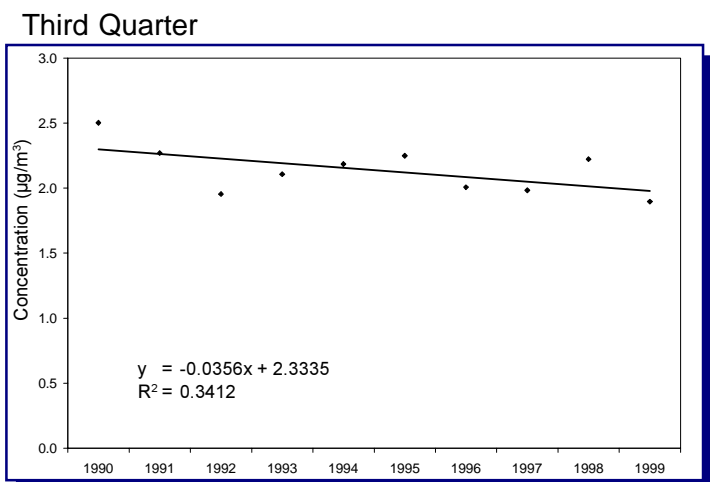
First Quarter



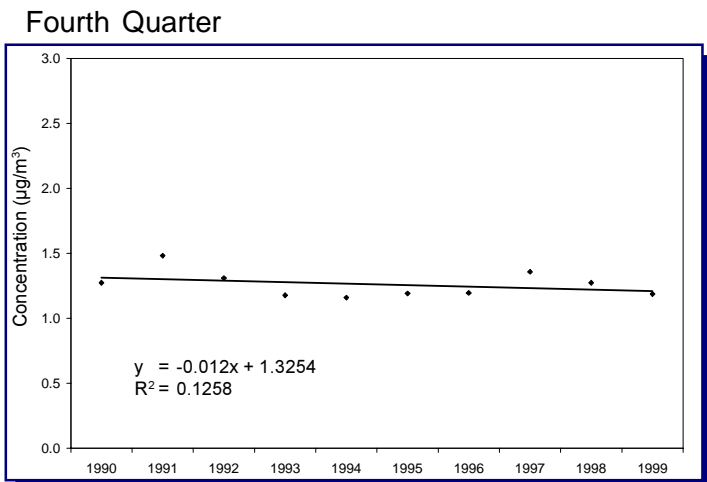
Second Quarter



Annual Average



Third Quarter



Fourth Quarter

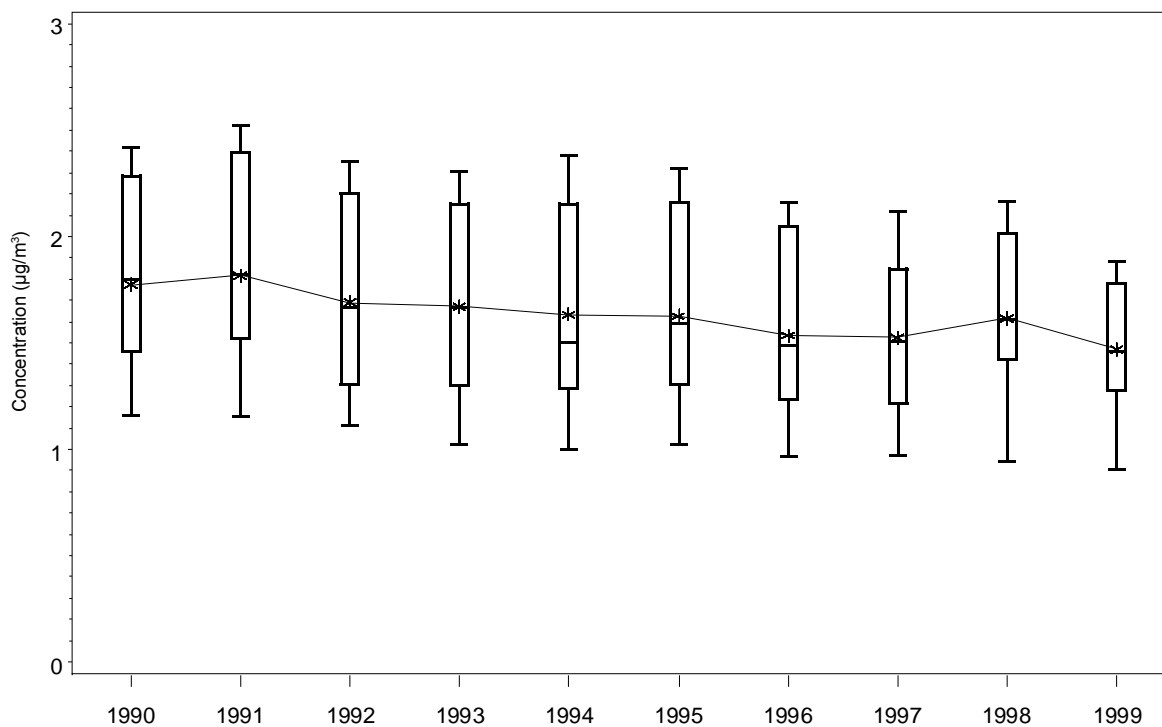
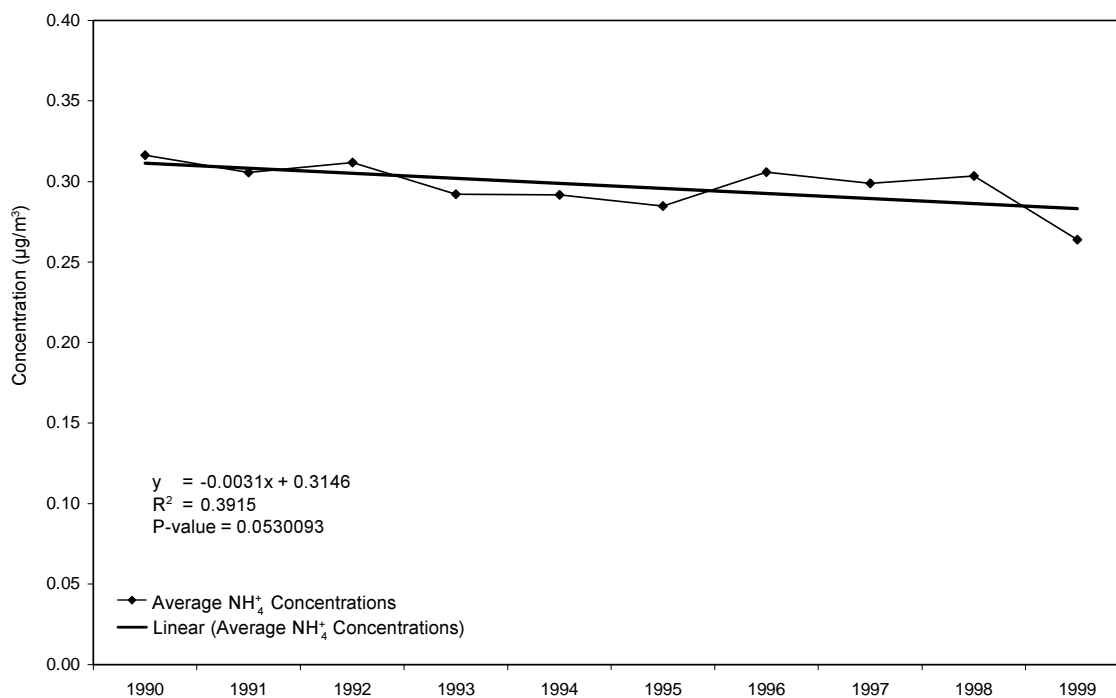
Figure 2-30. Trends in Composite Annual NH_4^+ Concentrations—Eastern United States**Figure 2-31.** Linear Regression Analyses for Annual Average NH_4^+ Concentrations—Western United States

Figure 2-32. Ratio of Nitrogen to Sulfur Concentrations (molar weights)

